



Experiment title:
Angular dependence of Ca K-edge XANES spectra in intercalated graphite compounds

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Local contact(s):
Fabrice Wilhelm

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Names and affiliations of applicants (* indicates experimentalists):

Delphine Cabaret, Geneviève Louprias and Christophe Bellin, IMPMC, University Paris 6

Nicolas Emery, Claire Hérold, J-F. Marêché and Philippe Lagrange, LCSM, University Nancy

Fabrice Wilhelm, Andrei Rogalev, ESRF

Report:

Superconductivity in graphite intercalation compounds (GICs) was subject of intensive studies during the late 80's and early 90's, due to their quasi-2D structure [1]. 40 years ago, some of GICs have been found superconducting, but at very low temperature, like KC_8 with $T_c=0.14\text{K}$ [2]. One year ago, superconductivity was discovered in YbC_6 (with $T_c=6.5\text{K}$) [3]. Then, we have demonstrated the existence of bulk superconductivity in CaC_6 [4] with a $T_c=11.5\text{K}$, and very recently we have succeeded in synthesizing **bulk $\text{Li}_3\text{Ca}_2\text{C}_6$** (β phase) [5], with a $T_c=11.15\text{K}$ [6]. These two last compounds exhibit the highest T_c , measured for GICs elaborated at ambient pressure, i.e. **almost 2 orders of magnitude larger** than in KC_8 . Recent *ab initio* calculations indicate the crucial role played by the charge in the intercalated Ca plane [7, 8]. The calculations [7] point at a BCS behaviour with a moderate electron-phonon coupling. The carriers are mostly electrons in Ca Fermi surface coupled with C phonons, perpendicular to graphene planes, leading to **superconductivity of Ca intercalant planes**. The role played by the intercalant non-complete ionization is pointed out by this **new scenario** and even **higher T_c** seem to be possible.

In order to investigate the full electronic structure of these two superconducting compounds, we have performed recent measurements at ESRF: Ca K-edge XANES spectra of CaC_6 , $\text{Ca}_2\text{Li}_3\text{C}_6$ and $\text{Ca}_3\text{Li}_{0.5}\text{C}_6$ have been measured on ID12 and CaC_6 Compton profiles have been measured ID15B, cf. Report HE 2135.

I. EXPERIMENTAL SETUP

The samples consist of three plates of intercalated graphites, synthesized by the Nancy's group, from highly oriented pyrolytic graphite (HOPG) [4]. The resulting compound is made of randomly oriented crystallites in the planes perpendicular to the **c**-axis (i.e. in a graphite plane) while they are highly oriented along their **c**-axis, allowing us to define its angle (0 or $\pi/2$) with the polarization vector $\mathbf{\epsilon}$. The plates are 3 mm side and

200 μm thick, with the c axis normal to the surface. Since the samples are reactive to ambient air, they were loaded in individual cell under argon atmosphere, and the cell were closed by kapton windows.

The sample cells were placed and **oriented in the beam line in such a way the angular dependence could have been measured without rotating them.** Therefore the sample surface exposed to the photon beam is the same for the two polarization vectors that have been selected. By so doing differences of self-absorption effects are avoided when recording the angular dependence. Details about the undulator, the energy calibration, etc, are missing in this report. The detection is achieved in fluorescence mode by seven Si photodiodes symmetrically placed around the photon beam.

Between 15 and 30 spectra were recorded for each polarization and each sample.

II. DETERMINATION OF THE SAMPLE ORIENTATIONS TOWARDS THE POLARIZATION VECTORS

For each sample, the absorption at the Ca K-edge has been measured for two distinct orientations of the polarization vector (called θ_1 and θ_2). The samples are supposed to be dichroic compounds. For any angle θ , being the angle between the high symmetry axis of the sample and the polarization vector ϵ , the absorption cross section is given, as a function of absorption cross-sections, by [9]:

$$\sigma(\theta) = \cos^2 \theta \sigma_{\parallel} + \sin^2 \theta \sigma_{\perp},$$

where σ_{\parallel} is the absorption cross section for ϵ along the symmetry c -axis.

The orientations of the single crystal towards the two ϵ_1 and ϵ_2 polarization vectors, called θ_1 and θ_2 respectively, were estimated using the following method. We used an oriented single crystal of calcite, CaCO_3 . Calcite crystallizes in the trigonal system, with $-3m$ point group. It is then also a dichroic compound [2]. For calcite, we recorded the Ca K-edge absorption signal for four distinct angles: θ_1 , θ_2 , $\theta = 0^\circ$ and $\theta = 90^\circ$. These two latter correspond to σ_{\parallel} and σ_{\perp} , respectively. The spectra are shown in figure 1. The θ angles ($i = 1, 2$) were then determined by a fit procedure. The fitting function is given by:

$$\sigma_i \equiv \sigma(\theta_i) = \alpha_i \sigma_{\parallel} + (1 - \alpha_i) \sigma_{\perp},$$

where $\alpha_i = \cos^2 \theta_i$, are the fitting parameters. In the above equation, the coefficients α_i were varied until the resulting spectrum coincide with experimental data $\sigma(\theta_1)$ and $\sigma(\theta_2)$, shown in fig.1. The results of the fitting procedure are shown in Table I and in figures 2 and 3.

$$\begin{aligned} \alpha_1 = 0.695 &\Rightarrow \theta_1 = 33.5^\circ \\ \alpha_2 = 0.29 &\Rightarrow \theta_2 = 57.5^\circ \end{aligned}$$

TABLE I: Results of the fitting procedure: orientation of the two polarizations vectors.

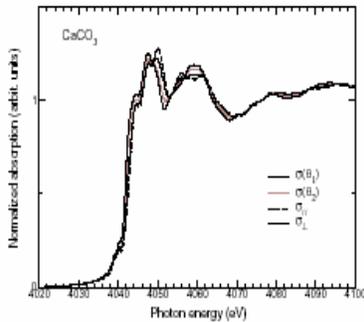


FIG. 1: Ca K-edge angular-dependent XANES spectra in an oriented single crystal of calcite.

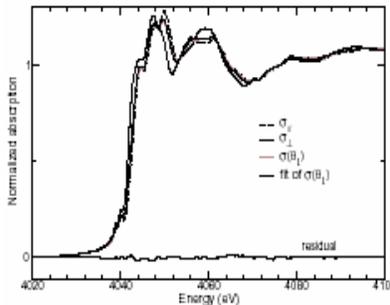


FIG. 2: Result of the fitting procedure of $\sigma(\theta_1)$

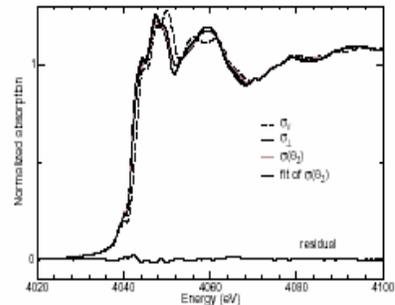


FIG. 3: Result of the fitting procedure of $\sigma(\theta_2)$

Fitting procedure results are shown in Table I and figs 2 and 3.

II. RESULTS AND DISCUSSION

For CaC_6 , 32 scans were recorded for each θ_1 and θ_2 orientations. Each scan comprises the seven signals recorded by the seven working photodiodes. We have looked carefully at the $7 \times 32 \times 2$ spectra. We have selected 19 scans for each polarization, a scan being the average of the seven signals. For $\text{Ca}_2\text{Li}_3\text{C}_6$, 17 scans were recorded for each θ_1 and θ_2 orientations. The resulting spectra are obtained by averaging 10 scans for each polarization. For $\text{Ca}_3\text{Li}_{0.5}\text{C}_6$, the non-superconducting α phase, 13 scans were recorded for each θ_1 and θ_2 orientations. The resulting spectra are obtained by averaging 5 scans for each polarization.

One can say the spectral shape of CaC_6 is rather different of the Li-bearing compounds, that are more similar. The spectra of CaC_6 do not exhibit the thin exciton peak around 4040 eV very well defined on the $\text{Ca}_2\text{Li}_3\text{C}_6$ spectrum. Instead the CaC_6 spectra present two distincts features. In addition, the **angular dependence of the Ca K-edge is found to be much more important in the superconducting materials.**

Using the evaluation of θ_1 and θ_2 from the CaCO_3 data, we are reconstructing absorption cross-sections for the three compounds.

Our preliminary calculations on CaC₆, using *ab initio* calculations [7], present a **good overall agreement** in terms of sign and shape of dichroic signal but not concerning the intensities of measured structures. Calculations are still in progress, taking into account, in particular, a better description of core-hole effects.

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